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硕 士 学 位 论 文

天然高分子新材料的制备及表征

Preparation and Characterization of Natural Polymer Based Novel Materials

段将将

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摘 要

现阶段，在环境污染和化石资源日益枯竭的双重压力下，人类社会发展遇到了前所未有的困境。天然高分子作为取之不竭、用之不尽的可再生资源，如何高效利用并开发高附加值产品，已成为国际前沿研究领域，受到越来越广泛的关注。特别是天然高分子官能团丰富、可降解、生物相容、无毒无害等卓越的性能，使其在污水处理、生物医学等领域具有巨大的应用价值。本文主要采用纤维素、壳聚糖、酪蛋白三种来源广泛的天然高分子作为原料，采用新型方法分别制备得到了 pH 敏感型再生纤维素分离膜、力学性能和耐酸性增强的壳聚糖吸附微珠、聚多糖多层水凝胶以及通过酪蛋白辅助制备得到的多级结构 ZnO 微球。具体研究结果如下：

pH 敏感型再生纤维素分离膜的制备、表征及应用研究

将溶解在 NaOH/硫脲新型绿色溶剂体系中的纤维素溶液在玻璃基板上流延，再将其浸渍在壳聚糖醋酸稀溶液中凝固再生，成功制备出了纤维素/壳聚糖复合膜。采用元素分析(EA)、差示扫描量热法(DSC)和傅里叶转换红外光谱(FTIR)对复合膜的组成进行了分析，证实了再生纤维素膜中壳聚糖的存在。衰减全反射傅里叶转化红外光谱(ATR-FTIR)和扫描电镜(SEM)显示壳聚糖分布在再生纤维素膜的表面；且与纯纤维素膜相比，复合膜的表面和断面显示出更加致密的均匀多孔结构，使得复合膜的机械性能比纯的纤维素膜有所提高。另外，利用微型平板膜设备，对该复合膜的纯水通量和对 Cu^{2+}的截留性能进行了测试。结果显示，该复合膜不但保持了较高的纯水通量水平；并且由于壳聚糖的引入，赋予了它极高的 Cu^{2+}截留性能；同时，对 Cu^{2+}截留性表现出 pH 敏感性。

力学性能和耐酸性增强的壳聚糖微珠的制备及表征研究

将 2 wt%的壳聚糖醋酸水溶液逐滴滴加到 0.5 wt%的纤维素 NaOH/硫脲水溶液中，成功制备出了表面包覆纤维素的壳聚糖微珠。采用 X-射线光电子能谱(XPS)对该复合微珠的表面组成进行了分析，证实了微珠表面纤维素的存在。采用 SEM 对微珠的表面及截面微观形貌进行了观测；结果显示，复合微球表面呈现多孔结构，该多孔结构是包覆于壳聚糖微珠表面的再生纤维素涂层的微观结构。由于微

珠的力学性能难以测试，因此，本部分工作采用相同的方法，制备成复合壳聚糖膜，进而对其的力学性能进行了表征；结果显示，与纯壳聚糖膜相比，复合壳聚糖膜的力学性能得到了增强。将壳聚糖微珠浸泡在 pH=2 的 HCl 的水溶液中，对其耐酸性进行了检测；结果显示，复合壳聚糖微珠的耐酸性与纯壳聚糖微珠相比，得到了改善。对 Fe^{3+}的吸附性能测试结果显示，表面涂覆纤维素后，壳聚糖微珠的吸附性能并没有受到影响。

聚多糖多层水凝胶的制备、表征及应用研究

利用 layer-by-layer (LbL)的方法，将含有交联剂的琼脂糖凝胶核在聚多糖水溶液和交联剂溶液中交替、反复浸渍，成功制备得到了聚多糖多层水凝胶。选用戊二醛和对苯二甲醛作为交联剂分别制备出了 pH 非敏感和 pH 敏感型壳聚糖多层水凝胶。采用壳聚糖单层水凝胶对壳聚糖多层水凝胶层厚控制因素进行了研究；研究结果显示，层厚增长是由交联剂在高分子溶液中的扩散过程决定的。按照相同的方法，选用 Al^{3+}作为交联剂制备出了羧甲基纤维素多层水凝胶。根据不同交联体系的结果，本部分工作对多层水凝胶形成机理进行了分析。采用 SEM 对壳聚糖和羧甲基纤维素多层水凝胶微观结构进行了观测；结果显示，壳聚糖和羧甲基纤维素多层水凝胶中各层均为网络大孔结构，且壳聚糖水凝胶每一层中又由若干亚膜层组成，其整体呈现多级多层结构。采用不同形状的凝胶核，能制备出各种形状的壳聚糖多层水凝胶。pH 敏感型壳聚糖多层水凝胶在较低 pH 介质中呈现 LbL 剥离式溶解过程。另外，将“洋葱状”壳聚糖多层水凝胶作为软骨细胞组织工程支架材料，并采用 SEM 观察软骨细胞在支架上附着和增殖，结果显示该材料具有良好的生物相容性。

酪蛋白胶束辅助多级结构 ZnO 微球制备及表征研究

将一定量的酪蛋白溶液、锌氨溶液以及无水乙醇按一定比例混合，得到的溶液通过水热法进行反应，成功制备出了由纳米 ZnO 颗粒组装而成的多级结构 ZnO 微球。该微球宏观尺寸范围为 500 nm-3 μm，构成它的纳米 ZnO 颗粒尺寸约为 30 nm。采用 X-射线粉末晶体衍射(XRD)对该多级结构 ZnO 微球的晶体结构进行了分析，表明其为典型的纤锌矿晶体结构。通过调控 Zn^{2+}浓度、氨水浓度、酪蛋白浓度以及无水乙醇浓度，对多级结构 ZnO 微球的制备条件进行了优化。通过升高水热反应温度，多级结构 ZnO 微球实现了从实心到空心的转化，并对空心

结构形成机理做出了解释，认为其是一种典型的奥斯瓦尔德熟化过程。通过对照实验，研究了酪蛋白、氨水对多级结构 ZnO 微球形成的贡献；研究了酪蛋白对 ZnO 晶体生长的调控机制。依据 FTIR 和热失重(TG)的结果，并结合海藻酸钠/氨水体系中制备得到的 ZnO 微球的结构差异，还对多级结构 ZnO 微球的自组装机理做了推论，认为多级结构 ZnO 微球是通过酪蛋白胶束与不同大小的 ZnO 纳米颗粒聚集体之间反复捕获、解脱，碰撞、融合过程中形成的。采用相同的方法，还成功制备得到了多级结构 CuO 微球。由此，本工作建立了一种在酪蛋白胶束/氨水体系中，通过水热反应，制备多级结构金属氧化物的简便方法。

本文制备、研究的天然高分子基新材料均属于原创性探索研究。

关键词:天然高分子 再生纤维素 壳聚糖 酪蛋白 复合材料 ZnO

Abstract

Today, the development of the human society has met serious difficulty at the challenges of environmental pollution and gradually exhausted fossil resources. Natural polymers, the renewable and clean resources, are fascinating and sustainable alternative energy resources. How to efficiently use them and to develop high-value materials from them have been becoming the global frontier research fields, which have attracted more and more attention. Because of the larger amount of functional groups, degradability, biocompatibility and non-toxicity, natural polymers have great potential application in fields such as wastewater treatment and biomedicine. In this work, cellulose, chitosan and casein were used as the raw materials. By empolying new methods, the pH-sensitive cellulose regenerated membrane, chitosan beads with improved mechanical properties and acid resistivity, polysaccharidesmulti-membrane hydrogels and hierarchical ZnO microspheres were prepared, respectively. The detail contents of our work are as follows:

Preparation, characterization and application of pH-sensitive regenerated cellulose membrane

Cellulose/chitosan hybrid membranes were successfully prepared by casting cellulose solution, which was dissolved in a NaOH/thiourea green solution system, onto the glass substrate and then regenerating it from chitosan (CS) acidic solution. The component of the hybrid membranes were characterized by elemental analyses (EA), Fourier transforms infrared spectra (FTIR) and differential scanning calorimetry (DSC), which indicated the CS existed in the regenerated cellulose membranes. The result of attenuated total reflection FTIR (ATR-FTIR) indicated the CS molecules were penetrated into the surface layer of the regenerated cellulose membrane. The scanning electron microscope (SEM) images of hybrid membranes display much denser homogeneous porous structures with mesh network patterns in the surfaces and cross-sections than those of pure regenerated cellulose membrane. As a result of the

denser structure, the strength of the hybrid membrane has been improved. In addition, the water permeability (*J*) and rejection (*R*) of Cu^{2+} for the membranes were determined by a mini flat membrane device. The results indicated the hybrid membranes not only maintains a high water flux, but also shows a high rejection of Cu^{2+}. At the same time, the hybrid membrane presents pH-sensitive on Cu^{2+} rejection.

Preparation and characterization of cellulose-coated chitosan beads with improved strength and acid resistivity

CS beads coated with cellulose were successfully prepared by simply dropping by dropping acidic CS solution into alkaline cellulose solution. The surface constitutes of prepared cellulose-coated CS beads were characterized by X-ray photoelectron spectra (XPS), which indicated that the cellulose exists in the surface of CS beads. The SEM images of composites CS beads exhibit porous structure in the surface, which is the microstructure of the covered regenerated cellulose layer. Compared with the pure CS beads, the composites CS beads display improved mechanical strength and acid resistance. However, the adsorption behavior of CS has not been reduced by the cellulose coating.

Preparation, characterization and application of a polysaccharides multi-membrane hydrogels

Polysaccharides multi-membrane hydrogels were successfully prepared by LbL methods. That was by immersing agarose gel-core containning crosslinking agent into biopolymers solution and crosslinking agent solution alternately and repeatedly. CS multi-membrane hydrogels with and without pH sensitivity were prepared by crosslinked with glutaraldehydeand and terephthalaldehyde, respectively. The factors of controlling layer thickness of CS multi-membrane hydrogels were studied by the CS mono-membrane hydrogels. The results indicated the layer thickness is controlled by the diffusion process of crosslinking agents into CS solution. In addition, carboxymethyl cellulose (CMC) multi-membrane hydrogel crosslinked with aluminium ion was also prepared by the same method. Summing up the results of different crosslinking system, the formation mechanism of multi-membrane hydrogels was explained. The microstructures of multi-membrane hydrogels, observed by SEM,

exhibit porous structures with mesh network patterns both in CS and CMC multi-membrane hydrogels. In addditon, it is notable that CS multi-membrane hydrogels consist of several sublayers in each layer and present hierarchical multi-membrane structureas in whole. Using flexible gel-cores, the various shapes of multi-membrane hydrogels, such as onion-like, tubular and star-like multi-membrane hydrogels were prepared. The decomposition studies showed that acid-sensitive CS multi-membrane hydrogels present LbL peeling off decomposition process. Finally, the properties of biomedicine of multi-membrane hydrogels were researched by culturing chondrocyte on CS multi-membrane hydrogel scaffolds. The SEM images displayed that the chondrocyte could excellently adhere and proliferate on the scaffolds after culturing two days.

Preparation and characterization of novel hierarchical ZnO microspheres

The hierarchical ZnO microsphere assembled by ZnO nanoparticles were successfully prepared by hydrothermal method with the assistance of casein micelles. The range of microspheres size is 500 nm-3 μm, and the size of ZnO nanoparticles is about 30 nm. The crystalline structures of hierarchical ZnO microspheres are in wurtzite phase, which were characterized by X-ray diffraction (XRD). The preparation conditions of ZnO microsphere were optimized through tuning the contents of Zn^{2+}, ammonia, casein micelles and ethyl alcohol. Through elevating reaction temperatures, the inner structures of ZnO microspheres were transformed from solid to hollow microsphere. We think the transformation is a typical Ostwald Ripening process. According to coordination chemistry theory and experiment results, the growth mechanism of ZnO crystals was investigated. The results indicated that the different ZnO crystals were formed due to the selective conjunction between casein micelles and ZnO microlites. Furthermore, according to the results of FTIR and Thermogravinetry (TG) and through comparing with the ZnO microspheres prepared in sodium alginate/ammonia system, we propose the self-assembly mechanism of hierarchical ZnO microspheres. That is the hierarchical ZnO microspheres are assembled by continually capturing and releasing between casein micelles and ZnO nanoparticles aggregates which themselves collide and fuse at the same time.

According to the same method, the hierarchical CuO microspheres were successfully prepared. Therefore, here, a facile method of preparing hierarchical metallic oxide materials is provided.

In this thesis, the preparations and characterizations of novel natural polymer materials are original researches.

Keywords: natural polymers; regenerated cellulose; chitosan; casein; composite materials; ZnO

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